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Zhang, Yang; Tang, Peter Torben; Hansen, Hans Nørgaard; Nielsen, Jakob Skov

Published in:

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Publication date:

2009

Document Version

Early version, also known as pre-print

[Link back to DTU Orbit](#)

Citation (APA):

Zhang, Y., Tang, P. T., Hansen, H. N., & Nielsen, J. S. (2009). Electroless Plating on Plastic Induced by Selective Laser Activation. In *Electroless Plating on Plastic Induced by Selective Laser Activation*

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Electroless Plating on Plastic Induced by Selective Laser Activation

Y. Zhang¹, P. T. Tang², H. N. Hansen¹, J.S. Nielsen¹

*1. Technical University of Denmark (DTU), Department of Mechanical
Engineering (DTU Mekanik), Produktionstorvet, Building 427S, 2800 Kgs.
Lyngby, Denmark*

2. IPU, Kemitovet 204, 2800 Kgs. Lyngby, Denmark

This paper presents a new method for selective micro metallization of polymers. A Nd:YAG laser is employed to draw patterns on polymer surfaces that are submerged in a liquid (usually water). After subsequent activation with palladium chloride and followed by auto-catalytic electroless plating, copper deposit only on the laser tracks. The mechanism of the palladium activation step is analyzed based on experimental results and theoretical calculations. It is believed that the laser introduces porous and rough structures on the surface, which favours the palladium attachment. Looking from the surface property's point of view, the basic polymer surface tends to attract palladium in an acidic solution. Using the laser treatment mentioned above, standard grades of thermoplastic materials such as ABS, SAN, PE, PC and others have been successfully metalized. The metalized tracks are down to 300 μm in width with 50 μm between two tracks, but further optimization is expected in this field. Due to the porous and rough structure of the laser track, excellent adhesion between metallization and substrate is obtained. On top of the first copper layer, additional metal such as nickel, gold, palladium or tin can be deposited.

For more information, contact:

Yang Zhang

Technical University of Denmark (DTU),

Produktionstorvet, Building 427S

2800 Kgs. Lyngby Denmark

TEL: +45 45254892

Email: yazh@mek.dtu.dk

1. Introduction

Moulded interconnect devices (MIDs) can be defined as thermoplastic components with electrical infrastructure (conductive tracks) or electrical components. MIDs are manufactured using a large variety of processes but what is common to all process chains is the use of injection moulding. Conventional injection moulding, two-component injection moulding, and insert moulding have all been reported¹ for this use. Another commonly used process for MID manufacturing is the laser direct structuring (LDS). LDS involves the use of special polymers (filled with organometallic complex or similar.) and a laser structuring process, followed by electroless plating in the laser treated areas.

Laser induced selective activation (LISA) is developed as a new technique that can do positional selective metallization of a polymer surface. As illustrated in figure 1 below, there are 3 primary steps included in the LISA process, (1). the polymer surface is modified by laser in a medium of deionized water, (2). the laser modified specimen is activated by submerging it in a palladium solution, and (3). the activated specimen is plated using electroless auto catalytic plating².

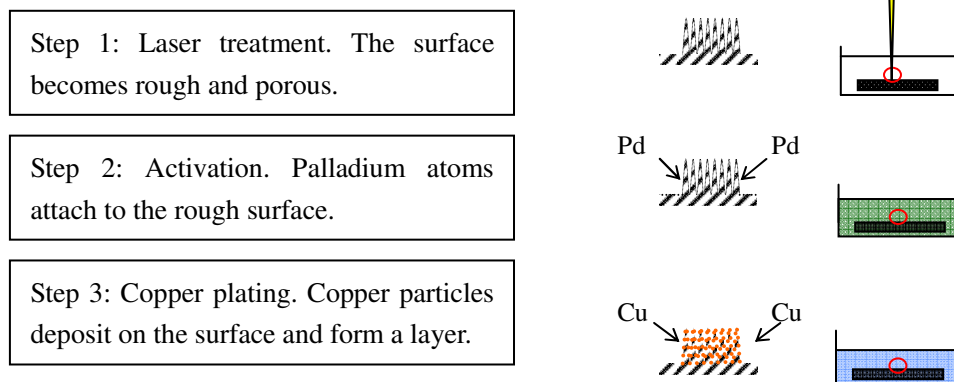


Figure 1: illustration of the main LISA steps.

The main difference between the LISA process and LPKF-LDS is that the polymer employed in LPKF-LDS needs to contain a special filler, such as an organometallic complex or an inorganic spinel compound. The laser beam will induce a physicochemical reaction with the filler and the resulting released metal atoms will act as the catalytic nuclei for electroless plating. This process, however, is expensive, since the entire polymer has to be filled with special

particles, while only the filler in the surface is used. Moreover, only relatively few polymer grades suitable for LDS are commercially available^{3,6}.

In an alternative process, the entire surface may be metalized first, and then, in later steps, the unwanted metal areas are removed for example by laser ablation, or photo lithography followed by etching, but these methods usually involve either toxic chemicals in the pre-treatment, such as chromic acid, or sputtering, and often lead to a substantial waste of metal since most of the metal layers are removed⁷. Table 1 makes a comparison between LISA and other techniques.

Table 1: LISA compared with other techniques.

	LDS	MIPTEC ⁷	Full-Metallization	LISA
Materials	Special filler in materials and only a few materials are available	Thermoplastic and ceramics	Thermoplastic	Common thermoplastic polymer
Laser	Special wavelength to crack the bonds, special laser head to shape the track	Special wavelength to remove the metal layer	Special laser wavelength to remove the metal layer	The laser energy can be absorbed by the materials
Wet step	Electroless plating	Electroplating and metal etching after sputtering	Dangerous chemicals for the pre-treatment	Activation and electroless plating

2. Mechanism hypothesis

The investigated substrate materials are injection moulded polymer, such as polycarbonate (PC) or polystyrene (PS). Black grades are preferred in the study for their good absorption of laser beam energy, but other colours can be used as well.

The work piece is machined by laser in a medium of deionized water. Deionized water is easy, safe, and cheap to get, and reduces the possibility of unknown reactions. Other types of liquids may also be used in the future and it may lead to different results.

In the laser machining step, the polymer surface will absorb the laser pulse energy in such a way that a thin layer on the surface melts. It is then instantly cooled down by the water surrounding it, so the polymer solidifies quickly and maintains a molten-like structure. After several passes (15-30 passes) of the laser, the surface will be full of peaks and pores due to the random distribution of the pulses. The roughness, or the surface structure of the track, is determined by the laser energy input.

During the activation step, the porous structure will keep some activation solution in the holes, in which palladium atoms attach to the surface. Then, when the sample is submerged in the copper bath, the copper solution will make contact with the palladium attached to the surface, causing copper to deposit on the palladium sites. After that, more copper will deposit and propagate to form a continuous layer. Also, copper particles are entangled with the surface material, creating a strong mechanical adhesion between the copper layer and the polymer surface. Lastly, one has to consider that if the standing peaks from the laser treatment are too high, it will take a long time for the copper layer to reach and cover the top. Therefore it is necessary to regulate the laser parameters such that the laser track's roughness and height is optimized in relation to both the adhesion force and plating time.

3. Experimental set-up

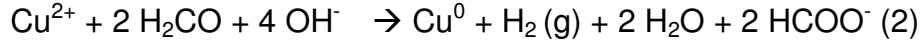
A lamp-pumped Q-switch Nd:YAG laser (wavelength 1064 μm [41840 μin]) was employed in the process. The laser beam traverses in a wobbly way, which increases the machined area. The beam velocity optimized for LISA is 60mm/s (2,63inch/s); and at the optimized setting, the average output power is around 3.4W.

The second step is the palladium (Pd) activation. Before the activation, the laser tracks must be completely wet by water. A fresh mixture of PdCl₂ and SnCl₂ solution is used as the activation bath, in which the chemical reaction as listed in formula (1) takes place⁴. During this step, reduced palladium atoms adhere to the laser modified surface, and become the active sites of copper growth in the subsequent plating step. The process takes 5 min, at room temperature, and the work pieces must be rinsed carefully by distilled water after this step.



The final step is the auto-catalytic electroless copper plating, according to the

reaction shown in formula (2)⁴. No external power supply is needed, as copper deposits on the activated sites of the surface. It takes 1 hour to get approximately a 5 μm (200 μin) thick copper layer. To prevent corrosion and oxidation and to be applicable for industrial use, a thin layer of nickel and gold can be deposited on top of the copper layer.



To decrease the plating time, the reactivation method was tried. After several minutes in copper bath, the work pieces were taken out and re-activated in the same activation bath for 5 min, and then they are put back to the copper bath again. In the reactivation, palladium deposits on the plated copper, so activated area is increased. Since copper grows faster on palladium than on itself, the plating time could be shortened.

To explore the copper deposition process, some tracks were only plated for a very short time, which is too short for Copper to cover all over, so Copper has just started to deposit on palladium atoms. Then, both the top view and the cross section view of those tracks were observed by scanning electronic microscope.

4. Results

After the laser treatment, the surface becomes spongy and porous, as shown in figure 2.

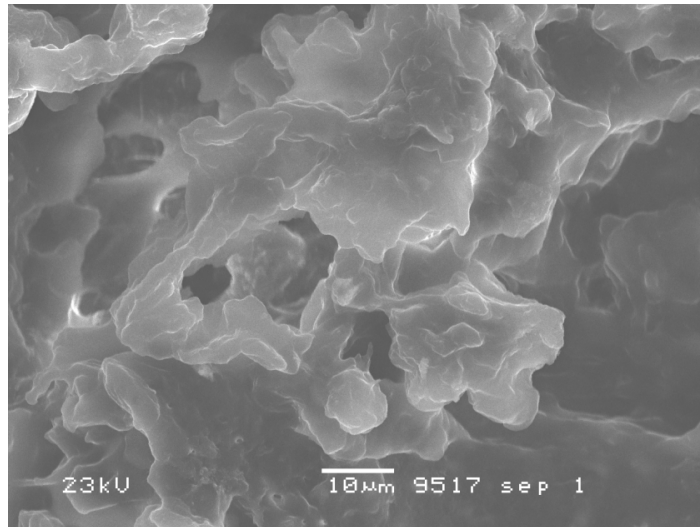


Figure 2: the spongy structure formed after the laser treatment on Polyethylene (PE) substrate.

The surface wetting property is obviously changed, as illustrated by the advancing contact angles measured by Dataphysics® contact angle system OCA series and related software SCA. The laser modified surface becomes much more hydrophobic than the original surface. The advancing contact angle of distilled water increased from 86°, on the original surface, to 146° on the laser modified area, as shown in figure 3. Therefore, if the laser tracks are completely dry before the activation, it becomes very hard to wet it again, and palladium has no entry to attach to the surface.

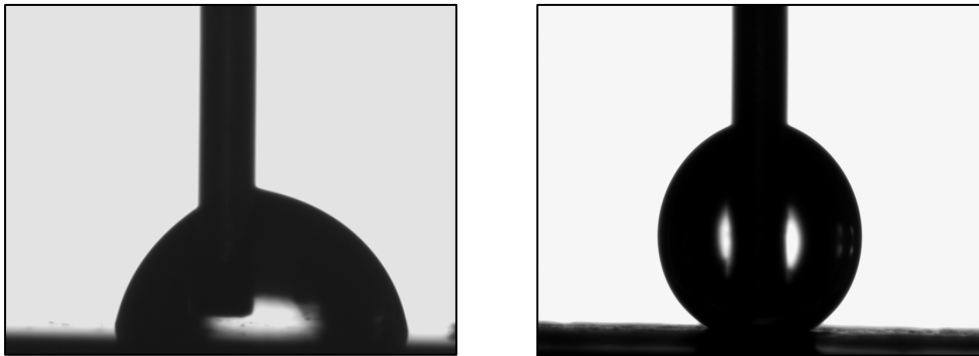


Figure 3: contact angle measurement on normal PC surface (left) and surface treated by laser (right).

Experiments showed that a completely dry sample needed at least 2 hours in the activation solution to achieve the same plating result compared to a sample that are not allowed to dry up after the laser machine. Therefore, it is highly desirable that the laser tracks are wet before the activation. The easiest method to keep the surface wet is to just store the species in water right after they are machined by the laser. One may also submerge the work pieces for 24 hours prior to the activation and plating.

After the activation, it is desirable that any activation solution outside the laser track is removed, because it can lead to metallization with weak-adhesion, and large area metallization may cause a plating bath collapse.

The reactivation method mentioned in section 3 increases the deposition speed effectively. If the plating was stopped after 2 minutes, and the surface gets reactivated for 5 minutes, then after another 43 minutes of plating, the copper layer was as thick as 4.8 μ m (188.9 μ in) averagely; While without reactivation, the thickness can only reach 2 μ m (78 μ in) in 45 minutes.

So far, the recommended plating procedures are:

- Wet the surface. Submerge the work pieces in water for 24 hours or in alcohol solution (>50%) for several minutes, if the laser track is dry.
- Wash the surface by sprayed alcohol, then by sprayed water, and submerged in a water tank for 1 minute.
- Activation for 5 minutes.
- Cascade rinsing carefully in distilled water.
- Copper plating for 1 hour or more, depending on the copper thickness to be achieved.

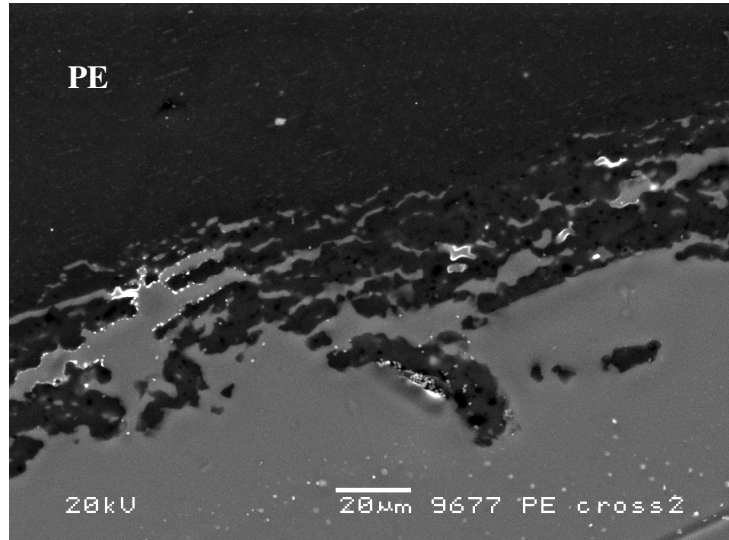


Figure 4: cross section of 1 minute plated PE.

To see how the copper propagates during the plating, laser tracks plated for 1, 2, and 3 minutes were observed by back scatter imaging using a scanning electron microscope (SEM), as shown in figure 4-9. The bright dots in the pictures are heavy elements, i.e. copper particles, in this case.

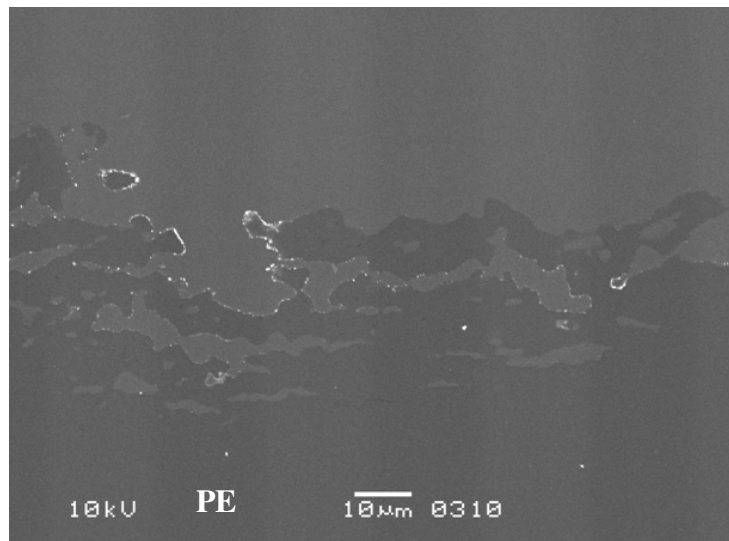


Figure 5: cross section of a 2 minutes plated PE.

Cross sections of the PE samples have a clear layered structure after laser treatment. figure 4 shows that after 1minute, copper started the deposition in the middle layers. In figure 5 it shows copper propagating along the top layer and in the 3rd minute, copper continued to grow along the surface top, while it also started to deposit at other sites in the middle layers, as depicted in figure 6.

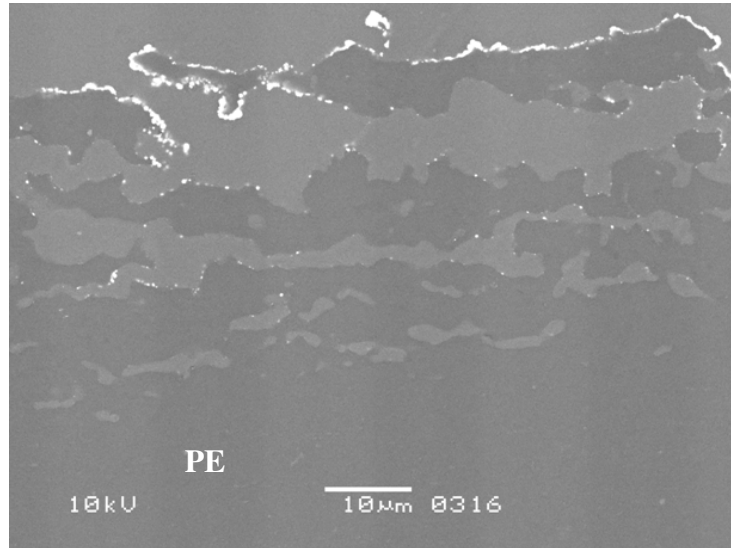


Figure 6: cross section of 3 minutes plated PE.

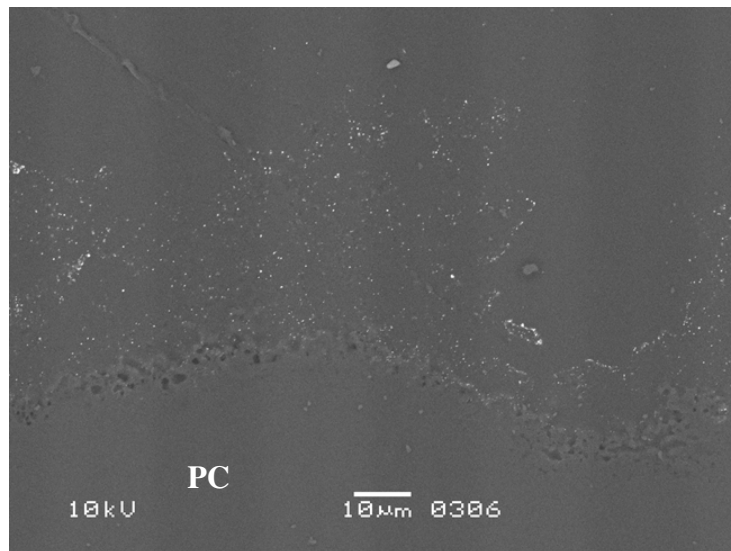


Figure 7: cross section of 2 minutes plated PC.

In the PC pictures, the layer structure is not obvious, but the deposition trend can be found clearly. Copper also preferred to grow along the surface top, since it's clear that figure 8 has more bright dots on top than figure 7. The figure 9 taken from top view of a 2 minutes plated PC piece also shows that

copper starts to deposit in a hole, not on the top.

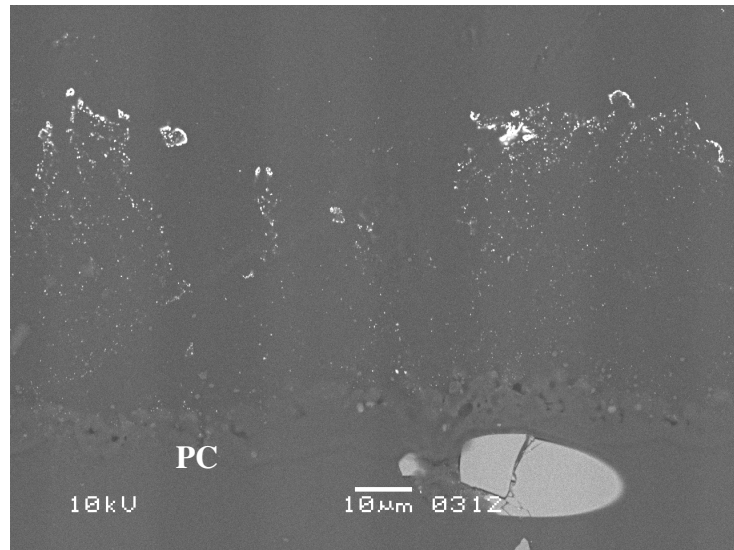


Figure 8: cross section of 3 minutes plated PC.

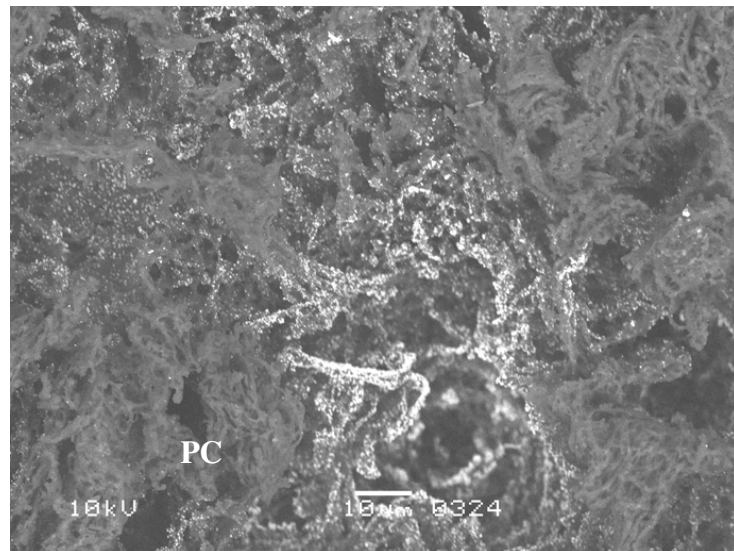


Figure 9: top view of 2 minutes plated PC.

As a primary examination for the adhesion strength, a tape test was administered and passed without problem. Then adhesion was measured by a by DFD® hydraulic tensile adhesion tester (PAT model GM01/6.3kN Adhesion Tester), the adhesion of the copper layer was as strong as 2.79MPa averagely, on PC substrate when the copper layer is 5µm (196.9µin) thick.

5. Conclusion

This paper introduced a new selective metallization method on polymer, which proved to be less toxic. In this method, less toxic chemical is used compared to other techniques such as laser ablation or 2k injection molding MID process. The plating copper bath employed in the plating step is a commercial product, which is easy to purchase. The laser used is also low power and standard. As a whole, the LISA process is cost efficient and environmentally friendly. A wide range of thermoplastic as well as standard laser equipments can be used to practice this technique, and it was demonstrated that the copper layer has a good adhesion to the substrate. The mechanism exploring work is partly done but still needs future attention.

6. Acknowledgements

The authors would like to acknowledge Monika Burimaite and Mikkel Østergaard Hansen in IPU, Katja Jankova, in Danish Polymer Center, Tobias Nørbo in Mechanical Engineering Department of DTU, and all the people who helped us in Department of Mechanical Engineering, DTU.

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